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The use of direct geometry spectrometers in molecular spectroscopy

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Abstract. The advantages and disadvantages of the use of direct geometry spectrometers for molecular spectroscopy and catalysis studies are described. We show that both direct and indirect geometry INS spectrometers are important tools for the study of industrially relevant areas such as catalysis, proton conductors and gas separation. We propose a novel hybrid instrument, Cerberus, that would offer high sensitivity and high-to-reasonable resolution across the entire ‘mid-infrared’ spectral range that would effectively advance research in these areas.

1. Inelastic neutron scattering spectroscopy

Inelastic neutron scattering (INS) spectroscopy [1] is a form of vibrational spectroscopy that is complementary to the conventional methods of infrared and Raman spectroscopies. Its usefulness derives from the properties of the neutron, which is a neutral particle of mass 1.00866 amu, almost identical to that of the hydrogen atom, 1.00794. The neutron has a magnetic moment, which has resulted in it becoming an essential tool for fundamental studies of magnetism [2]. Neutrons are scattered by atomic nuclei *via* the strong force and since the nucleus is only ~0.1% of the diameter of the atom, neutrons are highly penetrating. The nuclear scattering also means that there are no symmetry-based selection rules, so in principle all modes are allowed in INS spectroscopy. The intensity, S , of an INS transition is given by [1]:

$$S(Q, n\omega_i) \propto \frac{(QU_i)^{2n}}{n!} \exp(-(QU_{\text{Tot}})^2) \sigma \quad (1)$$

Where ω_i is the i th mode at transition energy ω , $n = 1$ for a fundamental, 2 for a first overtone or binary combination, 3 for a second overtone or ternary combination *etc.*..., Q is the momentum transfer defined as:

$$Q = k_i - k_f \text{ where } k \equiv 2\pi / \lambda \quad (2)$$



k (\AA^{-1}) is the wavevector; λ (\AA) is the wavelength of the neutron. The dependence of the scattered intensity on, and hence access to, Q is a major distinction between INS spectroscopy and infrared and Raman spectroscopies that only observe modes at $Q \approx 0$. U_i is the root mean square displacement of the atoms in the mode. σ is the inelastic scattering cross section of the atom and this is both element and isotope specific and is ~ 20 times larger for ^1H than any other nucleus (including ^2H). Hydrogen is the lightest element, consequently its amplitude of vibration (U_i) is the largest of any element. This fact combined with the large cross section means that the scattering from hydrogenous materials is dominated by modes that involve motion of hydrogen. The exponential term in equation (1) is a Debye-Waller factor, U_{Tot} is the total root mean square displacement of all the atoms in all the modes, (both internal and external), and its magnitude is in part determined by thermal motion. This can be reduced by cooling the sample and so spectra are typically recorded below 30 K.

2. Indirect and direct INS spectrometers

The first INS spectrometer was the triple axis spectrometer and was invented by Bertram Brockhouse in 1952, as described in his Nobel lecture [3]. This type of instrument, which is still in use today [4], employs monochromators to fix both k_i and k_f , thus it is enormously flexible and can (theoretically) access any point in (Q, ω) space. The strength of the instrument is also its Achilles heel: spectral acquisition is by a point-by-point method and is very slow. The throughput can be greatly increased by fixing either k_i or k_f and using a ‘white’ beam in the scattered or incident neutrons respectively. Instruments that fix k_i or known as direct geometry instruments and those that fix k_f as indirect geometry instruments.

Historically, indirect geometry instruments have been used for problems that do not involve magnetism. Thus most studies in molecular spectroscopy and catalysis have used such instruments. The reasons for this are instructive. Figure 1 compares the INS, Raman and infrared spectra of N-phenylsuccinimide (the structure is shown as an inset to the figure), a model compound for bismaleimide composites. All three spectra are similar in appearance, so anyone familiar with infrared or Raman spectra can understand the INS spectrum. The complementarity of all three spectra is clear: features that are strong in one spectrum may be weak or absent in the others, thus the out-of-phase carbonyl stretch at 1700 cm^{-1} is very strong in the infrared, weak in the Raman and absent in the INS. Conversely, the out-of-plane carbonyl bend at 407 cm^{-1} is strong in the INS, weak in the Raman and

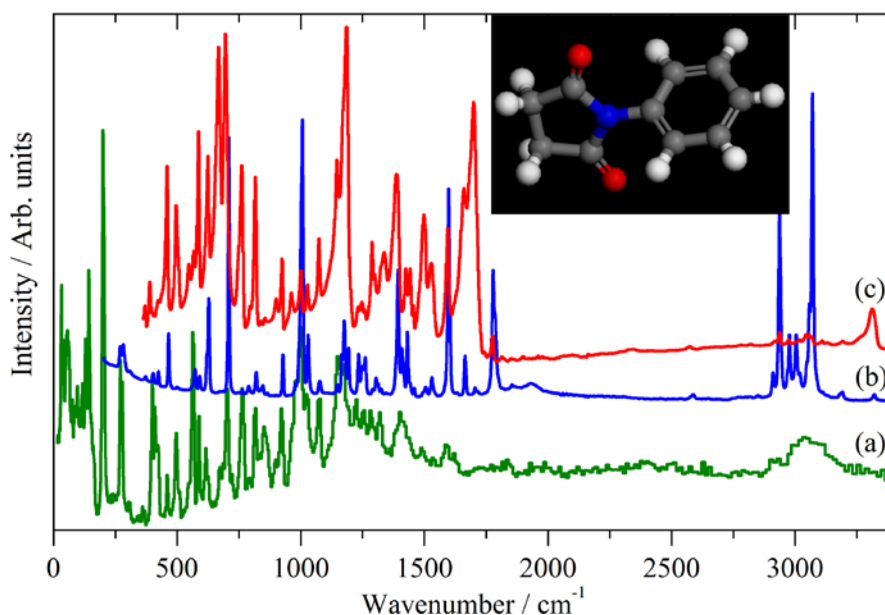


Figure 1. Vibrational spectra of N-phenylsuccinimide: (a) INS recorded on TOSCA at 20 K, (b) Raman and (c) infrared at room temperature.

absent in the infrared. The transition energies are the same in all three spectra, since these are a molecular property, however, the intensities differ since the interactions between the probe and the molecule are different in all three cases. The Raman spectrum cuts-off at 200 cm^{-1} and the infrared at 370 cm^{-1} while the INS spectrum extends to almost 0 cm^{-1} . This is a region that can be observed by Raman and infrared spectroscopies but it becomes increasingly difficult (and costly) as 0 cm^{-1} is approached. The availability of a wide spectral range is particularly useful in studies of supported metal catalysts where the absorption of light by the support results in a spectral cut-off that can be as high as 1400 cm^{-1} . For INS spectroscopy, this is irrelevant and most support materials *e.g.* alumina, silica, carbon, are transparent and the entire spectral range is accessible. Indirect geometry INS spectrometers are generally simple to operate with few user inputs required. For the last decade or so, TOSCA at ISIS has been the world's best spectrometer of this type, this dominance is being challenged by the new instruments VISION at SNS and IN1-Lagrange at ILL. All three instruments are described in detail elsewhere in this volume.

Direct geometry spectrometers have only recently started to be exploited for 'non-magnetism' investigations. There are several reasons why this has occurred. The first is availability. Figure 2 shows the distribution of direct and indirect INS spectrometers and there are significantly more direct geometry spectrometers, particularly those with high resolution and wide spectral range. This pattern is likely to continue, the European Spallation Source has proposed four direct geometry spectrometers and only two indirect geometry spectrometers. (A complete description of the instruments available at neutron facilities can be found via <http://neutronsources.org/neutron-centres.html>).

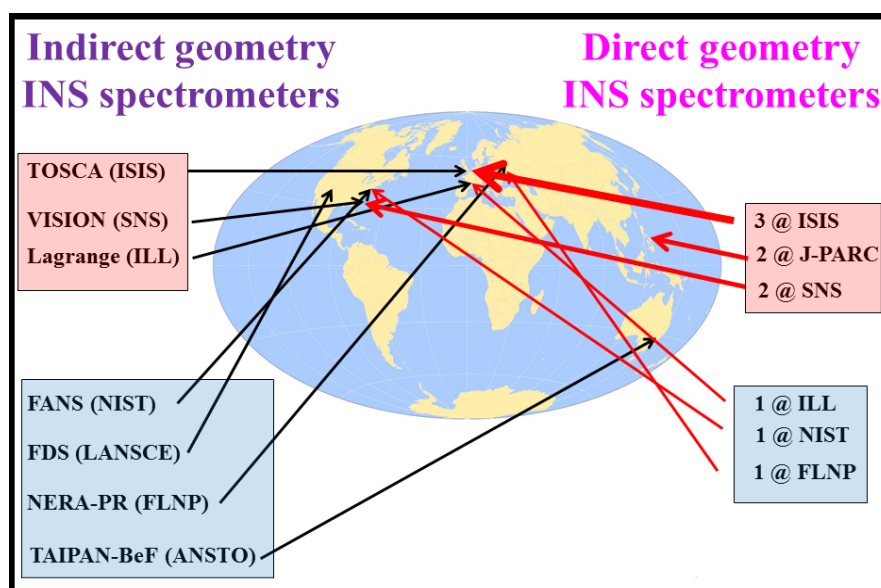


Figure 2. Distribution of INS spectrometers. Those in the pink boxes offer high resolution and wide spectral range, those in the blue, lower resolution and/or a restricted spectral range.

A second reason is that direct geometry instruments have large detector areas which makes them very sensitive. Thus MAPS [5] at ISIS has $\sim 16\text{ m}^2$ of detector area, in contrast TOSCA has $\sim 0.4\text{ m}^2$. This results in a significant advantage for MAPS as shown in figure 3. It can be seen that there is a about a factor of three in signal-to-noise ratio in favour of MAPS. If the resolution is relaxed on MAPS [5] then the difference increases to ~ 10 . If lower resolution can be employed then MERLIN [6] at ISIS is almost tenfold more sensitive than MAPS, by virtue of a larger solid angle of detection and greater incident flux by use of a guide, as shown in recent work on hydrocarbon overlayers on

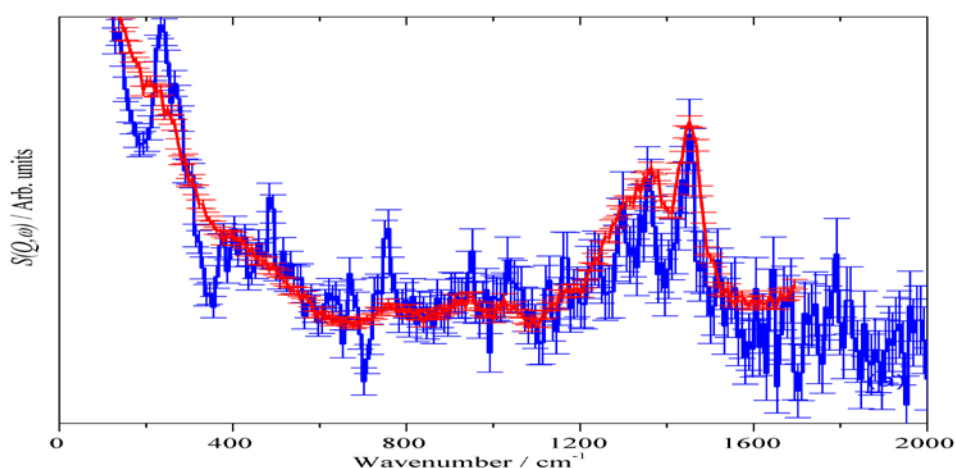


Figure 3. Comparison of the spectra recorded on MAPS (red) and TOSCA (blue) from the same sample.

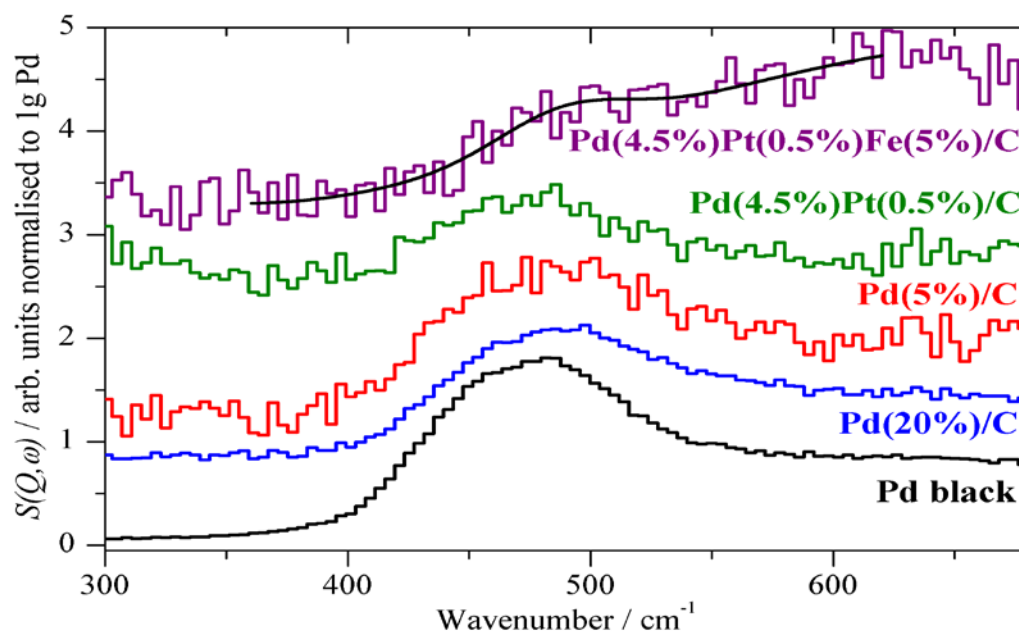


Figure 4. Comparison of the INS spectra recorded on MAPS at 20 K of a series of palladium-based catalysts [8] that are relevant to the hydrogenation of nitroarenes to aminoarenes. The peak at 480 cm⁻¹ is due to β-PdH. The carbon support and the empty sample can have been subtracted from the spectra.

catalysts [7]. Supported metal catalysts with realistic metal loadings of 1-5 wt% typically have < 1 mol% of hydrogen present, which is the detection limit on TOSCA. The improved sensitivity of the direct geometry instruments means that it is possible to study such systems. An example is shown in figure 4 for a series of palladium-based catalysts [8] that are relevant to the selective catalytic hydrogenation of nitroarenes to aminoarenes for use in polyurethane manufacture. A key parameter is the amount of hydrogen available from the catalyst *via* storage as β-PdH. Even for supported nanoscale ternary alloy particles as found in the industrial PdPtFe/C catalyst, it is still readily detectable at the lowest level.

The sensitivity advantage is likely to become less important with time as the latest generation of indirect geometry spectrometers, VISION at SNS and IN1-Lagrange at ILL, are optimised to have a very large detected flux.

Perhaps the key difference between direct and indirect geometry spectrometers is that the former can access a much larger range in Q and, crucially, can always access smaller Q . This is shown in figure 5 which shows the (Q, ω) plot for iodomethane (methyl iodide, CH_3I) recorded with incident energies (E_i) of 4840 and 2017 cm^{-1} . The purple and green lines show the trajectories of the forward and backscattering banks on TOSCA, however, all low final energy indirect spectrometers follow trajectories that lie either on or between those shown. Thus there is essentially no Q -resolution, so it is not possible to scan Q at fixed energy transfer on any operating indirect spectrometer. It can be seen that large energy transfer involves large momentum transfer. The importance of this arises from equation (1), since higher order transitions, *i.e.* $n \geq 2$, depend on Q^{2n} these become significant at large Q and, in particular, phonon wings (combinations between internal modes and the external density of states) become very strong. In parallel there is an overall dampening of intensity caused by the Debye-Waller factor. The combination of these two processes means that the fundamental transitions are largely swamped by the nearby higher order processes, rendering them unobservable. With a direct geometry spectrometer, by only using the detectors in forward scattering *i.e.* at low Q , high energy transitions are readily observable. This is illustrated in figure 6, where the data for $4 \leq Q \leq 10 \text{ \AA}^{-1}$ obtained from figure 5 is compared to the spectrum of iodomethane recorded on TOSCA. From the TOSCA spectrum, figure 6a, it would be assumed that the arrowed peak at 3043 cm^{-1} were the unresolved C–H stretch modes. Inspection of the MAPS spectrum, figure 6d, has considerably better signal-to-noise ratio and shows a peak at 2948 cm^{-1} (arrowed) that is not apparent in the TOSCA data. In fact, this peak is the unresolved C–H stretch modes, the peaks at 3043, 3161, 3272 cm^{-1} are combinations of the C–H stretch and the intense librational mode at 112 cm^{-1} ($\text{CH} + \text{lib}$, $\text{CH} + 2 \times \text{lib}$, $\text{CH} + 3 \times \text{lib}$ respectively).

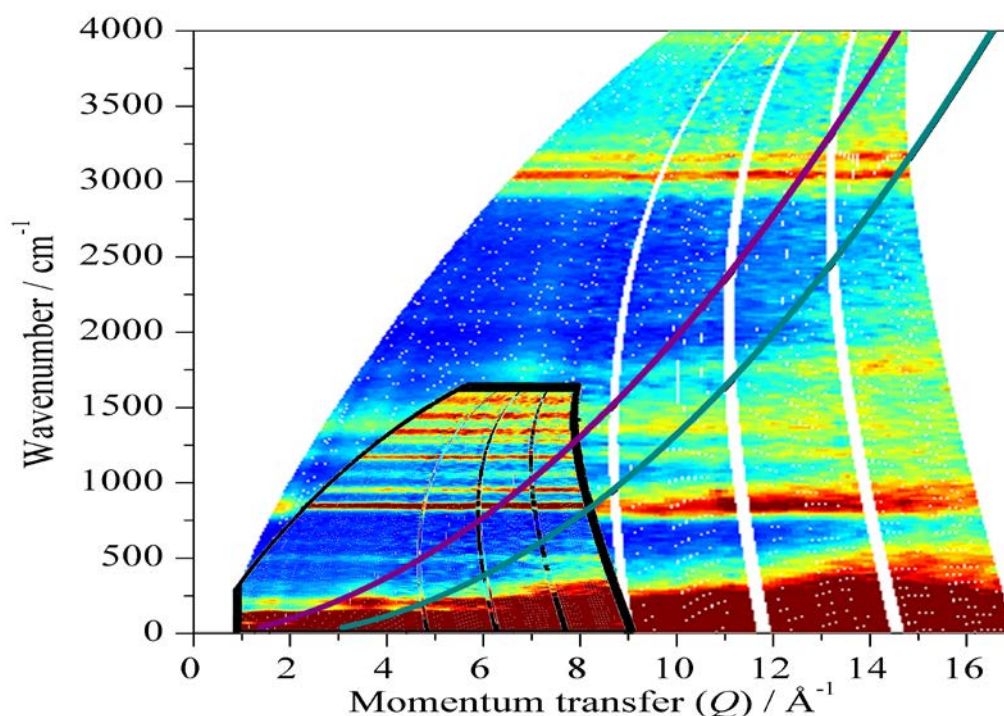


Figure 5. (Q, ω) plot of iodomethane recorded on MAPS at 20 K with incident energies of 4840 and 2017 cm^{-1} . The solid lines are the trajectories of an indirect geometry instrument with a final energy of $\sim 40 \text{ cm}^{-1}$ for scattering angles of 45° (purple trace) and 135° (olive trace).

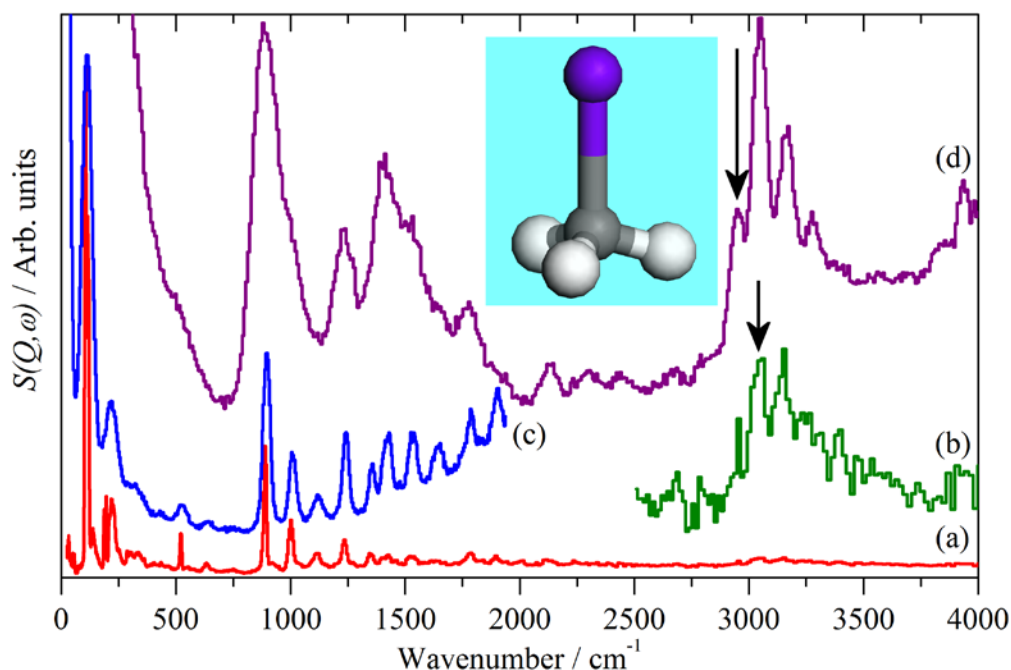


Figure 6. INS spectra of iodomethane recorded at 20 K on (a) TOSCA, (b) TOSCA $\times 10$ ordinate expansion of the 2500 – 4000 cm^{-1} region, (c) and (d) MAPS with incident energies of 4840 and 2017 cm^{-1} respectively. (c) and (d) are the data shown in figure 5 summed for the detectors at $4 \leq Q \leq 10 \text{ \AA}^{-1}$.

3. The next generation - Cerberus

Figures 5 and 6 illustrate the advantages of direct geometry spectrometers: high signal-to-noise ratio, wide Q range and, especially, access to small Q . In addition to extending the useful energy transfer range, variable Q also enables higher order processes, $n \geq 2$, to be distinguished [9] from fundamentals $n = 1$, *via* equation (1). Reducing the magnitude of the Debye-Waller factor by using small Q makes experiments at room temperature and above possible [10], where our experience on TOSCA has shown that this is not useful on indirect geometry instruments.

While there are undoubted advantages to direct geometry instruments, there are also drawbacks. The most serious of these is illustrated in figure 6. Practically, for a direct geometry instrument the best resolution is obtained when the energy transfer is close to the incident energy and degrades with decreasing energy transfer, thus for figure 6d, the width of the features around 3000 cm^{-1} is $\sim 60 \text{ cm}^{-1}$ (1.2% of E_i) whereas for the feature at $\sim 900 \text{ cm}^{-1}$ it is 140 cm^{-1} (2.9% of E_i). The width of the latter is entirely due to resolution broadening, as the width measured with 2017 cm^{-1} incident energy is 38 cm^{-1} (1.9% of E_i) and by TOSCA is 14 cm^{-1} . Thus to obtain a high resolution measurement across a wide spectral range, several spectra with different $\text{cm}^{-1} E_i$ are needed and these are difficult to merge because of the varying resolution functions. In contrast, the complete spectrum is obtained in one pass with an indirect geometry instrument, in this case the resolution degrades with increasing energy transfer, E_T .

There is a further disadvantage with direct geometry instruments, their very sophistication means that they require significant user input. Thus at ISIS the variables are:

- Choice of instrument ($\times 3$ @ ISIS)**
- Choice of Fermi chopper slit package ($\times 3$ @ MAPS)**
- Choice of Fermi rotation speed ($\times 11$ @ MAPS)**
- Choice of incident energy (120 – 16000 cm^{-1} @ MAPS)**

(Similar considerations apply for the SNS and J-PARC). Whereas on TOSCA the only decision is how long to measure for!

It is apparent that there is considerable complementarity between direct and indirect geometry instruments and this is particularly manifested for molecular spectroscopy and catalysis studies. It would be doubly advantageous to combine both types of operation in a single instrument. This would enable studies across the full spectral range to be performed without the need to transfer (or prepare new) samples between instruments, increasing both efficiency and the certainty that the same material is being measured on both instruments.

Figure 7 shows a conceptual diagram for such an instrument – Cerberus. This instrument would be optimised for sensitivity while maintaining reasonable resolution. The instrument would sit at 12 m and view an ambient temperature water moderator with a state-of-the-art neutron guide. For indirect geometry, it would use the large collection area analysers developed on VISION at SNS in 135° backscattering. This would provide a resolution of $\sim 2.25\% E_T$, (*c.f.* TOSCA $\sim 1.25\% E_T$). In forward scattering at 45° would be either more high resolution modules or, to provide sensitivity at the cost of resolution, would be analyser modules that each consist of a cooled beryllium + graphite filter. These would be designed such that they can also operate in a beryllium-only mode to further increase the bandpass and hence flux. The effect on the resolution is shown in figure 8, it can be seen that even at the lowest resolution there is still useful information to be obtained.

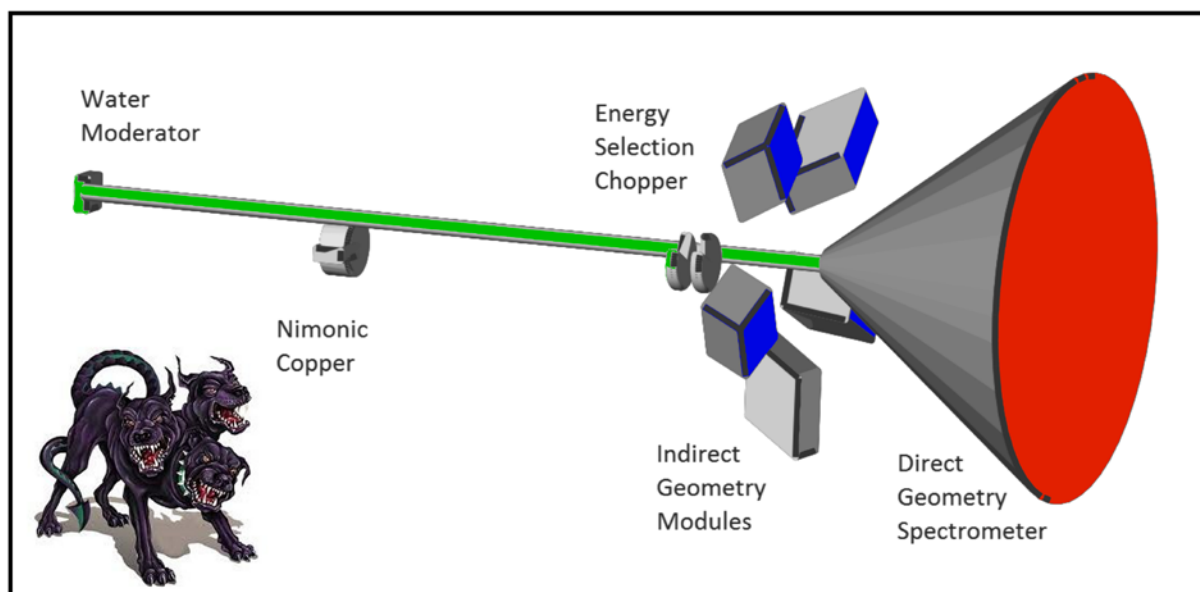


Figure 7. The key components of Cerberus showing the indirect geometry detectors in backscattering (blue) and the area detector in forward scattering for use in direct geometry and diffraction.

Also in forward scattering at 2.5 m from the sample will be a large area detector (angular range of $\pm 30^\circ$ horizontal and vertical) that will be used in conjunction with a Fermi chopper in the incident beam, which will be moved out of the beam when the instrument is in indirect geometry mode, note that measuring spectra in the indirect and direct modes is not possible simultaneously. In indirect mode this detector will function as a low resolution, high count-rate diffraction detector, which will complement a high resolution diffraction detector sited in near-perfect backscattering. The direct geometry forward scattering detectors should offer the same energy resolution as the equivalent area on MERLIN, which we have shown is sufficient to distinguish aliphatic and aromatic C–H stretch modes [7]. To reduce the cost, the detector need not be position sensitive. Experience has shown that Q -resolution in the C–H/N–H/O–H stretch region (which is what this detector is needed for) is not essential as all the detectors are summed to improve the signal-to-noise ratio.

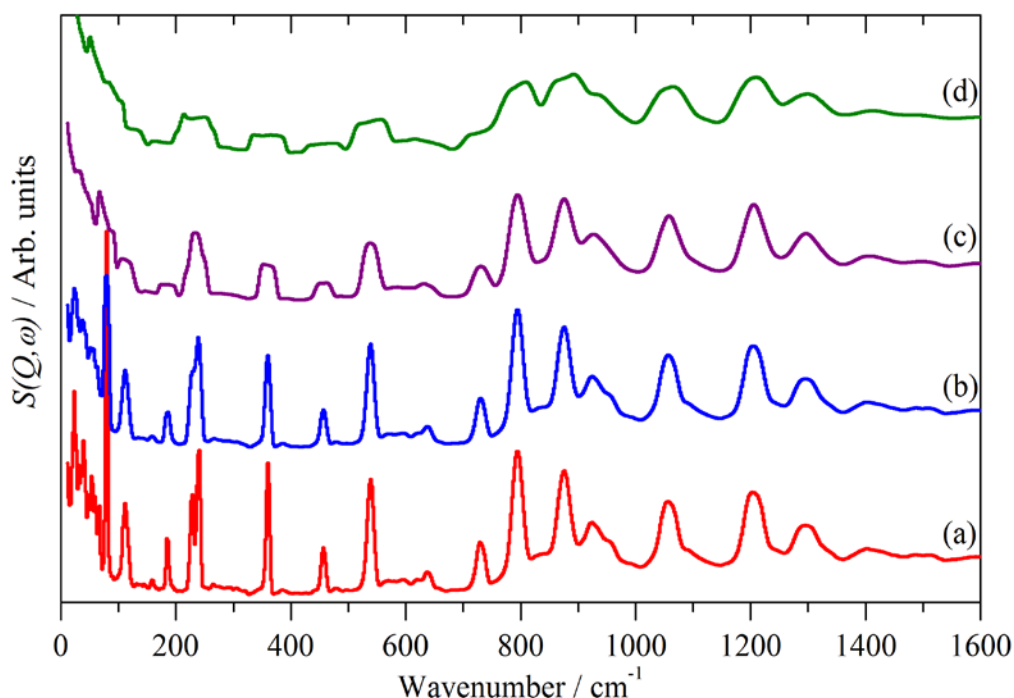


Figure 8. Simulation of the effect on the resolution on the INS spectrum of 2,5-diiodothiophene by the use of high throughput detector banks on Cerberus. (a) Experimental TOSCA spectrum, (b) simulated for 12 m incident flight path (high resolution banks), (c) simulated for Be + C banks and (d) simulated for Be only banks.

There are three fields where Cerberus would have an immediate impact: (1) catalysis, (2) proton conductors and (3) gas separation and storage.

(1) Much of catalysis is concerned with the transfer of hydrogen between reagents and products and Cerberus is ideally suited to these type of studies. For the first time it will enable good resolution data to be collected on the same sample across the entire energy range. Access to the C–H/N–H/O–H stretch region provides a very simple means of identification and is ideally suited to quantitation of the species present [11]. The 0 – 2000 cm⁻¹ region is where the details of the catalyst-adsorbate interaction can be discerned and the indirect backscattering detectors provide the good energy resolution needed for this. However, the surface species of interest are often present in low concentration and good resolution is of no use if there is insufficient sensitivity. This problem is addressed by the indirect forward scattering which will provide at least a tenfold increase in sensitivity and possibly as much as a 100-fold increase over the backscattering detectors. The improved sensitivity will also allow industrially important non-hydrogenous adsorbates, such as CO_x, NO_x and SO_x to be studied by INS for the first time.

(2) Proton conductors are heavy metal oxides that are hydrated to generate mobile hydroxyls and have considerable potential in intermediate temperature fuel cells. These materials exhibit multiple sites for incorporation of hydroxyls, thus diffraction studies are only able to provide an average picture of the material, the crucially important local structure around the hydroxyl groups is lost. Spectroscopy provides this missing local picture and INS is particularly matched to these needs as the low energy modes that (in conjunction with first principles modelling) enable discrimination between the various possible sites are easily observed [12]. These modes are often weak or obscured to optical probes. Access to the O–H stretch region is needed to quantify the species present and to discriminate between hydroxyl groups and water.

(3) Gas separation is becoming an increasingly important activity with the major driver being the need to separate CO₂ from waste streams. Recent work on TOSCA has shown that it is possible to detect changes in materials caused by SO₂ or CO₂ gas absorption [13] but that it is at the limits of sensitivity of the instrument. The increased flux of Cerberus will enable such studies to become routine.

4. Conclusions

In this paper we have highlighted the advantages and disadvantages of the use of direct geometry spectrometers for molecular spectroscopy and catalysis studies. To date, these instruments have not been extensively used for such studies but they are likely to comprise an increasingly important component of the workload on such instruments. At ISIS this is already happening; currently on MAPS ~25% of beamtime is non-magnetism, whereas five years ago it was almost zero.

It has become clear that both direct and indirect geometry INS spectrometers are important tools for the study of industrially relevant areas such as catalysis, proton conductors and gas separation. We strongly believe that these areas could be very effectively addressed by a novel hybrid instrument, Cerberus, that would offer high sensitivity and high to reasonable resolution across the entire ‘mid-infrared’ spectral range.

Acknowledgments

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